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 European Patent Office  
 Office européen des brevets

(11) Publication number:

**0 158 271**  
A2

(12)

# EUROPEAN PATENT APPLICATION

(21) Application number: 85103998.2

(51) Int. Cl.<sup>4</sup>: C 23 C 8/36

(22) Date of filing: 02.04.85

(30) Priority: 05.04.84 JP 68208/84

(43) Date of publication of application:  
16.10.85 Bulletin 85/42

(84) Designated Contracting States:  
CH DE FR GB IT LI SE

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(54) Process for ion nitriding aluminum or aluminum alloys.

(57) A process for ion nitriding aluminium or an aluminium alloy as an article to be treated, in which: the article is disposed in a sealed vessel; the oxygen gas in the vessel is removed; the surface of the article is heated to a prescribed nitriding temperature; the surface of the article is activated to facilitate the formation of an aluminium nitride layer by the subsequent nitriding treatment; and thereafter the article is subjected to ion nitriding, thereby forming an aluminium nitride layer having excellent wear resistance and high hardness. This ion nitriding treatment for aluminium material can be carried out even at temperatures lower than a solution treatment temperature of aluminium material.

EP 0 158 271 A2

85/8733 EPC

1 TITLE OF THE INVENTION

PROCESS FOR ION NITRIDING ALUMINUM OR ALUMINUM ALLOYS

5 BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a process for ion  
10 nitriding aluminum or aluminum alloys.

Description of the Prior Art

Since aluminum and aluminum alloys (hereinafter  
referred to as aluminum material) have low hardness and poor  
15 wear resistance, attempts have been made to develop surface  
treating methods for improving these properties. However,  
aluminum material has strong affinity to oxygen in the air  
and combines readily with oxygen to form a stable, dense and  
thin layer of alumina( $\text{Al}_2\text{O}_3$ ) thereon. Therefore, the sur-  
20 face treating method for aluminum material has limitations,  
as compared with surface treatment of iron or ferrous  
alloys, and only such surface treatment as formation of an  
alumina coating film by anodic oxidation has been put into  
practice. However, the alumina coating film merely has a  
25 Vickers hardness of about 200 to 600 (variable with the  
treating conditions) and thus it has not sufficient wear  
resistance.

1       On the other hand, as a coating film having higher  
hardness than that of the alumina coating film, there is an  
aluminum nitride(AlN) coating film. Aluminum nitride is  
useful since it is stable up to a very high temperature of  
5 2000°C or above and has excellent wear resistance, high  
thermal conductivity and good insulating properties.

Aluminum has strong affinity to nitrogen and combines  
readily with nitrogen to form aluminum nitride. Therefore,  
attempts have been made for forming aluminum nitride on the  
10 surface of aluminum material. For example, there are a  
melting method in which a part of aluminum material as a  
material to be treated is melted and nitrified, a reactive  
sputtering or reactive vapor deposition method, and the  
like. However, in the melting method, the material to be  
15 treated is deformed through melting and the obtained alumi-  
num nitride layer has a Vickers hardness as low as 200 or  
less. Further, the reactive sputtering or vapor deposition  
method has drawbacks such as poor adhesion between the alu-  
minum nitride layer and the material to be treated, dif-  
20 ficulty in treating many articles and high treating cost.

For realizing a method not using the melting method and  
enabling the treatment of many aluminum articles, there was  
an attempt to apply an ion nitriding method for treating  
iron or ferrous alloys to the formation of an aluminum nitride  
25 coating film having excellent wear resistance. However, such  
attempt has been found difficult because of an alumina layer  
easily formed on an aluminum article to be treated as men-  
tioned above.

1       A nitriding treatment for aluminum articles of a plate-  
shaped or rod-shaped form has not been possible because alumi-  
num material easily reacts with oxygen to form an alumina  
( $\text{Al}_2\text{O}_3$ ) layer thereon before nitriding as mentioned above. It  
5 has only been possible to obtain AlN powder by heating alumi-  
num or aluminum alloy powder in a nitrogen or ammonia  
atmosphere. However, this method requires much expense and  
time. Further, it cannot be applied to direct nitriding  
treatment of aluminum articles having a plate-shaped or rod-  
10 shaped form.

#### SUMMARY OF THE INVENTION

Accordingly, it is an object of the present invention to  
15 provide a surface treating method for improving wear  
resistance of aluminum material.

It is another object of the present invention to provide  
a surface treating method for forming an aluminum nitride  
layer of high hardness on the surface of aluminum material.

20       It is a further object of the present invention to pro-  
vide a process for ion nitriding aluminum material which can  
be effected even at low temperatures such as its solution  
treatment temperature or below.

Other objects, features and advantages of the present  
25 invention will become apparent from the following description  
when taken in connection with the accompanying drawings.

The process for ion nitriding aluminum or an aluminum  
alloy according to the present invention comprises: disposing

1 aluminum or an aluminum alloy as an article to be treated in a  
sealed vessel; removing residual oxygen gas in the sealed  
vessel; heating the surface of the article to a prescribed  
nitriding temperature by introducing a gas for heating into the  
5 sealed vessel and providing electric discharge; activating the  
surface of the article by introducing a gas activation into the  
sealed vessel and providing electric discharge; and ion  
nitriding the surface of the article by introducing a gas for  
nitriding into the sealed vessel and allowing discharge in  
10 the vessel.

This process enables the formation of an aluminum nitride  
layer having high hardness and excellent wear resistance on  
the surface of an aluminum or aluminum alloy article.

Further, the aluminum nitride layer formed is a coating  
15 layer relatively uniform and having good adhesion.

The ion nitriding treatment according to this invention  
can be carried out at a temperature not exceeding the solution  
treatment temperature (about 550°C) for aluminum material.  
Therefore, the nitriding treatment can be applied to an alumi-  
20 num article without deforming the same.

#### BRIEF DESCRIPTION OF THE DRAWINGS

The drawings show examples of the invention.

25 Fig. 1 is a schematic view illustrating an ion nitriding  
apparatus used in Example 1 according to the present  
invention;

Figs. 2 and 3 relate to the layer formed on an

1 aluminum or aluminum alloy article treated in Example 1, Fig.  
2 is a microphotograph (magnification x1000) showing the  
metallic structure of the section of the treated article and  
Fig. 3 is an electron probe microanalysis (EPMA) chart of alu-  
5 minum and nitrogen components in the surface of the article;  
and

Figs. 4 and 5 relate to the aluminum nitride layer of  
articles treated in Example 4 showing wear loss of the treated  
articles.

10 DETAILED DESCRIPTION OF THE INVENTION

In the ion nitriding process of the present invention,  
aluminum or an aluminum alloy as an article to be treated is  
disposed on a jig such as a stand or a hanger installed in a  
15 sealed vessel (the disposing step). Aluminum alloys to be  
used in this invention contain aluminum as its main component  
and at least one of chromium, copper, magnesium, manganese,  
silicon, nickel, iron, zinc or the like.

Then, the sealed vessel is closed tightly and the residual  
20 oxygen gas in the vessel is removed (the oxygen gas removing  
step). For removal of the residual gas, a vacuum pump such as  
a rotary pump or diffusion pump is used and the reduction in  
pressure and the replacement of the residual gas by an intro-  
duced gas are repeated. In this process, as an gas to be  
25 introduced, hydrogen gas, a rare gas or the like is used. It  
( $1.33 \cdot 10^{-6}$  bar)  
is preferred that the reduction in pressure is  $10^{-3}$  Torr/or  
less, because it becomes difficult to form an aluminum nitride  
( $1.33 \cdot 10^{-6}$  bar)  
layer having good adhesion when it exceeds  $10^{-3}$  Torr. It is

0158271

- ( $1.33 \cdot 10^{-8}$  bar)  
1 further preferred that the reduction in pressure of  $10^{-5}$  Torr/  
or less is attained by using a diffusion pump so that the  
layer having more excellent adhesion can be formed. In  
reducing the pressure, the furnace is heated by a heater  
5 installed in an inner wall of the furnace.

- Next, the surface of the article is heated to a  
prescribed nitriding temperature by introducing a heating gas  
into the sealed vessel having the reduced pressure and causing  
discharge (the heating step). In this step, it is preferred  
10 to use hydrogen gas, nitrogen gas or a rare gas such as helium  
gas as a heating gas. These gases accelerate the heating of  
the article to be treated while minimizing damages of the  
article due to ion bombardment. Further, the heating gas is  
ionized by discharge and the accelerated particles collide  
15 with the surface of the article to purify the surface by  
removing substances consisting of organic compounds such as  
carbon and oil on the surface of the article. In this step,  
direct current glow discharge, alternating current glow  
discharge such as high frequency discharge, or the like may be  
20 employed. The direct current glow discharge is preferred in  
view of low cost and a large heating capacity.

- It is preferred that the pressure of a hermetically  
( $1.33 \cdot 10^{-6}$  bar to  $1.33 \cdot 10^{-2}$  bar)  
sealed vessel is from  $10^{-3}$  to  $10$  Torr/. In particular, it is  
preferable that the pressure is from  $10^{-2}$  to  $10$  Torr/ in the  
( $1.33 \cdot 10^{-5}$  bar to  $1.33 \cdot 10^{-2}$  bar)  
25 case of direct current glow discharge and from  $10^{-3}$  to  $10^{-1}$   
( $1.33 \cdot 10^{-6}$  bar to  $1.33 \cdot 10^{-4}$  bar)  
Torr/ in the case of alternating current glow discharge. That  
is because the discharge becomes unstable when the pressure is  
small or than the above-mentioned range and the temperature  
distribution of an article to be treated becomes non-uniform

1 when the pressure is larger than the above range.

In this step, the surface temperature of an article to be treated is heated to a nitriding temperature. However, if the temperature is also raised in the subsequent activating step,  
5 the surface of the article may be heated to the nitriding temperature minus a temperature rise in the subsequent step.

Then, the surface of the article to be treated is activated by introducing an activating gas into the sealed vessel and causing discharge (the activating step). This step is a  
10 pretreatment for promoting the reaction velocity in the subsequent nitriding treatment. Namely, it is carried out in a manner to activate the surface of the article so that aluminum nitride is formed readily in the nitriding treatment. In this step, substances which are still existing on the surface of  
15 the article to be treated as a barrier restraining nitriding are removed or changed in quality into a state where they do not obstruct the nitriding. Such substances include aluminum oxide ( $\text{Al}_2\text{O}_3$ ) and substances adhering to the surface of the article such as organic substances which cannot be removed  
20 even by the purifying action in the heating step. Of these substances, aluminum oxide ( $\text{Al}_2\text{O}_3$ ) is formed readily as a stable, dense and thin (several nm ) film layer on the surface of the article even when the article is left at a room temperature, because aluminum has high affinity to oxygen and  
25 the both combine with each other easily. Since the alumina layer cannot be sufficiently removed in the heating step, it is reduced, removed, or changed in quality by ion bombardment of activating gas in this activating step, thereby to activate the surface of the article to be treated.



1       The activating gas for use in this step may be one or  
more rare gases of helium(He), neon(Ne), argon(Ar),  
krypton(Kr), xenon(Xe) and radon(Rn). The use of these rare  
gases enables high activation of the surface to be treated  
5   with efficiency.

Usually, in the activating step, direct current glow  
discharge or alternating current glow discharge such as high  
frequency discharge is employed, but ion beam sputtering may  
be employed. Of these, direct current glow discharge is pre-  
10   ferred in view of low cost, efficiency in the removal of  
nitriding restraining substances and a large heating capacity.

The sealed vessel preferably has a pressure of from  $10^{-3}$   
( $1.33 \cdot 10^{-6}$  bar to  $6.67 \cdot 10^{-3}$  bar)  
to 5 Torr/. In particular, it is preferred that the pressure  
( $1.33 \cdot 10^{-5}$  bar to  $6.67 \cdot 10^{-3}$  bar)  
of the vessel is from  $10^{-2}$  to 5 Torr/ with direct current glow  
( $1.33 \cdot 10^{-6}$  bar to  $1.33 \cdot 10^{-4}$  bar)  
15   discharge and from  $10^{-3}$  to  $10^{-1}$  Torr/ with alternating current  
glow discharge. That is because the discharge becomes  
unstable with the smaller pressure due to arc generation or  
the like and a smaller amount of nitriding restraining  
substance can be removed with the larger.

20       In carrying out the activation step, a heating gas is  
changed to an activating gas with the discharge continued.  
However, another method may be adopted, in which the discharge  
is once interrupted simultaneously with stopping the introduc-  
tion of a heating gas, the heating gas is removed, and then an  
25   activating gas is introduced into the vessel to a prescribed  
pressure to restrict the discharge.

The surface of an article to be treated may further be  
heated in this step where necessary.

1 Further, the activating step as a pretreatment for the  
subsequent ion nitriding step may be carried out before the  
above-mentioned heating step. However, if the heating step  
takes a long time, the effect of the activating step will be  
5 lowered. That is because an alumina layer is formed on the  
surface of the article to be treated due to a very small  
amount of residual oxygen in the sealed vessel and a very  
small amount of oxygen or oxidizing gas in the atmosphere (a  
heating gas) during the heating step.

10 Then, an ion nitriding step is preformed by introducing a  
nitriding gas into the vessel and generating glow discharge in  
the vessel (the ion nitriding step).

As a nitriding gas for use in the ion nitriding step,  
nitrogen( $N_2$ ) or a gas with a nitrogen base, e.g., ammonia( $NH_3$ )  
15 or a mixed gas of nitrogen( $N_2$ ) and hydrogen( $H_2$ ) is used. When  
the mixed gas is used, it is preferred that the mixed gas has a  
high content of nitrogen. That is because the use of high  
purity nitrogen contributes to a rapid formation of aluminum  
nitride and obviates disadvantages such as corrosion of an  
20 inner surface of a sealed vessel.

Further, as the glow discharge, direct current or alter-  
nating current glow discharge is used.

It is preferred that the pressure of the vessel is from  
( $1.33 \cdot 10^{-4}$  bar to  $2.66 \cdot 10^{-2}$  bar)  
10<sup>-1</sup> to 20 Torr/. The formation speed of aluminum nitride,  
25 i.e. the nitriding speed is low under the lower pressure and  
the glow discharge becomes unstable under the higher pressure.

A treating temperature in the ion nitriding step is pre-  
ferably set to be in the range of from 300 to 500°C. The

1 nitriding speed is low with the treating temperature less than  
300°C, and melting and deformation (e.g. change in dimensions  
and generation of distortion) of an article to be treated is  
caused with the treating temperature exceeding 500°C. Further,  
5 under higher temperatures, spalling of an aluminum nitride  
layer is apt to occur during cooling. It is more preferred  
that the treating temperature is from 450 to 520°C.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

10 Examples of the invention are described hereinafter.

##### Example 1

An aluminum nitride layer was formed on an aluminum  
article by ion nitriding according to the invention and the  
thickness of the aluminum nitride layer was measured.

15 In this Example, the ion nitriding apparatus shown in  
Fig. 1 was used. The apparatus comprises, as its main com-  
ponents, a hermetically sealed vessel 1 of stainless steel and  
a holder 2 installed at the middle of the vessel. The sealed  
vessel 1 is composed of a lid 1a and a reaction furnace 1b,  
20 the former having a window 11 and the latter a preheating  
heater 12 on its inner side surface. Further, a stainless  
steel anode plate 13 is installed on the inner side of the  
heater 12. The bottom part of the sealed vessel 1 is provided  
with a gas introducing pipe 14, a gas exhausting pipe 15, a  
25 supporting pillar 21 for the holder 2, a cooling water pipe 16  
for feeding cooling water to the pillar 21 and a mercury mano-  
meter 17.

1       The gas introducing pipe 14 is connected through control  
valves to a high purity nitriding gas bomb and a high purity  
hydrogen gas bomb (both are not shown). Further, a vacuum pump  
3 is connected to the gas exhausting pipe 15.

5       A direct current circuit 4 as the cathode is formed between the anode 13 and the holder 2. The current of the direct current circuit 4 is controlled by an input from a dichromatic thermometer 41 for measuring the temperature of articles to be treated so that the current circuit 4 functions to maintain the  
10 temperature of articles within a given range.

      In this Example, two industrial pure aluminum plates (discs having aluminum content of over 99.5%, an outer diameter of 19 mm and a thickness of 10 mm) were used as articles to be treated and they were disposed on the holder 2, as shown in  
15 Fig. 1.

      For ion nitriding with the apparatus, articles to be treated were disposed on the holder, and the sealed vessel was tightly closed. Then, the vessel was reduced in pressure by the vacuum pump up to the residual gas pressure of  $10^{-3}$  Torr/  
20       Thereafter, the furnace wall was heated with the preheating heater for 30 minutes while the residual gas was being sucked by the vacuum pump. Immediately after the heating, hydrogen gas was introduced into the sealed vessel until the pressure of 4  
      (5.33·10<sup>-3</sup> bar) Torr/ was reached to replace the residual gas with hydrogen, and  
25       then the gas pressure in the vessel was reduced to  $10^{-3}$  Torr/  
      (1.33·10<sup>-6</sup> bar) again. Such replacement with hydrogen gas was repeated two or three times so as to remove the residual gas in the furnace as much as possible.

0158271

Then, hydrogen gas was allowed to flow through the furnace (1.33·10<sup>-6</sup> bar) having the reduced pressure of 10<sup>-3</sup> Torr/ while the gas in the furnace was being sucked by a vacuum pump so that the pressure (1.73·10<sup>-3</sup> bar) in the furnace was maintained to be 1.3 Torr/. Then, direct current voltage of several hundred volts was applied across the two electrodes 13 and 2 to start electric discharge and to heat articles to be treated by ion bombardment. When the surface of each article was heated up to 500°C, the flow of hydrogen gas was stopped and subsequently argon gas was introduced. The introduction of argon gas was controlled so as (1.33·10<sup>-3</sup> bar) to have the argon gas pressure of 1 Torr/ in the furnace and then the discharge was continued further for 2 hours with the (1.33·10<sup>-3</sup> bar) argon gas pressure maintained at 1 Torr/. In another method, electric discharge is interrupted simultaneously with stopping the flow of hydrogen gas and then the residual hydrogen gas is removed, followed by the introduction of argon gas to restart the discharge.

Sputtering for treating the articles by the discharge in the argon gas atmosphere was carried out at 500°C for 2 hours.

20 Then, the introduction of argon gas was stopped and nitrogen gas was introduced into the furnace. The flow of nitrogen gas was controlled to maintain the nitrogen gas pressure in the furnace at  $3.5 \text{ Torr}$  and, after the temperature of article to be treated was set at a prescribed nitriding temperature as shown in Table 1, ion nitriding of the articles was carried out for 5 hours maintaining the nitriding temperature. It is preferable to continue the discharge when argon gas is changed over to nitrogen gas.

After the nitriding treatment, the discharge was ceased

0158271

1 and the articles were allowed to cool under reduced pressure  
 of about  $10^{-3}$  Torr<sup>(1.33·10<sup>-6</sup> bar)</sup>. After the articles were cooled to below  
 50°C, they were taken out of the furnace. The thus treated  
 articles had black layers formed thereon.

5 Each black layer obtained was tested for material identi-  
 fication by a X-ray diffraction method and, as a result, every  
 layer was confirmed to be aluminum nitride (AlN) of wurtzite  
 type.

10 Table 1

	Test No.	Activation process Gas for activation	Nitriding temp. (°C)	Layer thick- ness (μm)	Hardness of matrix (kg/mm <sup>2</sup> )	Surface hardness including nitrided layer (kg/mm <sup>2</sup> )
15	1	Ar	300	0.2	45	55
	2	"	350	0.5	39	60
	3	"	400	0.8	37	73
	4	"	450	1.8	32	102
20	5	"	475	2.5	29	265
	6	"	500	3.0	27	360
	7	"	525	5.1	27	700
	8	"	550	7.5	26	1200
	9	"	600	Spalling	24	Unmeasurable
	10	"	650	Spalling	23	"
25	C <sub>1</sub>	H <sub>2</sub>	400	No nitriding	36	-
	C <sub>2</sub>	"	550	"	25	-
	C <sub>3</sub>	"	600	"	24	-

0158271

1        Then, the thickness of black layers formed on the surface  
of the articles and the surface hardness of the same were  
measured. The results are shown in Table 1. The specimen of  
Test No. 6 treated at a nitriding temperature of 500°C was cut  
5 and a microphotograph (magnification x1000) of Fig. 2 shows  
its section. In addition, the elemental analysis of the  
section was carried out by an EPMA method and the result is  
shown in Fig. 3. The surface layer was confirmed to be a hard  
aluminum nitride layer by these tests.

10       Further, for comparison, ion nitriding treatment tests  
were carried out by the same method as the above-mentioned  
except the use of hydrogen gas as the activating gas in the  
activation process (Test Nos. C<sub>1</sub>-C<sub>3</sub>). As a result, articles  
of Test Nos. C<sub>1</sub>-C<sub>3</sub> were not nitrided.

15

#### Example 2

Industrial pure aluminum plates (disks having aluminum  
content of over 99.5%, an outer diameter of 19 mm and a thickness  
of 10 mm) were treated using the ion nitriding apparatus used  
20 in Example 1.

The nitriding treatment for the articles to be treated in  
Example 2 was similar to that in Example 1. Therefore, differ-  
ences between the two are described.

In Example 2, as the activating gas in the activation  
25 process, helium(He) gas, neon(Ne) gas or argon(Ar) gas was used.  
( $1.33 \cdot 10^{-4}$  bar)  
The pressure of these introduced gases was each 0.1 Torr, and  
sputtering was carried out at 500°C for 1 hour under an atmos-  
phere of the introduced gas.

0158271

1 Further, the ion nitriding in the ion nitriding step was carried out at 500°C for 5 hours.

Thus, a black layer was formed on the surface of each article treated.

5 Each black layer obtained was tested for material identification by X-ray diffraction analysis and, as a result, every layer was confirmed to be aluminum nitride(AlN). Further, the aluminum nitride layer was measured for thickness. The results are shown in Table 2.

10

Table 2

Test No.	Activation process Gas for activation	Layer thickness ( μm )
11	He	2.1
12	Ne	2.5
13	Ar	3.2

15

### Example 3

20 Disk-shaped members having an outer diameter of 19 mm and a thickness of 10 mm made of industrial aluminum alloys JIS (Japanese Industrial Standards) 2017 (Test No. 14) and JIS 6061 (Test No. 15) were used as articles to be treated.

The ion nitriding treatment in Example 3 was similar to that in Example 1. Therefore, differences between the two are 25 described.

In this Example, argon(Ar) gas was employed as an activating gas, the pressure of the introduced gas was set to be  $0.79 \cdot 10^{-3}$  bar) 0.6 Torr/.



0158271

1 and sputtering for the surfaces of articles was carried out  
by the discharge in an atmosphere of the introduced gas at  
500°C for 1 hour.

As a nitriding gas for use in the ion nitriding step,  
5 ammonia(NH<sub>3</sub>) gas and a mixed gas of nitrogen(N<sub>2</sub>) and hydrogen  
(H<sub>2</sub>) were each used, and the nitriding was carried out under  
treating conditions as shown in Table 3.

Thus, a black layer of aluminum nitride(AlN) was formed  
on the surface of each article. The thickness of aluminum  
10 nitride layers thus obtained was measured. The results are  
shown in Table 3.

Table 3

Test No.	Nitriding-treating conditions			Layer thickness ( μm )
	Nitriding gas	Gas pressure (bar) Torr	Treatment temp.(°C)xtime(hr)	
14	NH <sub>3</sub>	(4.67·10 <sup>-3</sup> ) 3.5	520x10	2.0
15	10N <sub>2</sub> +H <sub>2</sub>	(4.67·10 <sup>-3</sup> ) 3.5	520x 6	1.5

20 Example 4

Two types of aluminum alloys in practical use were used  
as articles to be subjected to ion nitriding and aluminum  
nitride layers thus formed were measured for thickness and  
tested for wear resistance.

25 The ion nitriding process and apparatus used in this  
Example were similar to those used in Example 1. Therefore,  
differences between the both are described in detail.

As articles to be treated, ring-shaped specimens having

1 an outer diameter of 20 mm, an inner diameter of 10 mm and a  
thickness of 10 mm made of a practically used aluminum alloy  
(duralmin JIS 2017:Test No. 16) and of a practically used Al-Si  
alloy [AA(Aluminum association) A390:Test No. 17] were used.

5 Argon(Ar) gas was used as the activating gas in this  
activation treatment. The introduced gas pressure in the  
activation treatment was  $0.6 \text{ Torr}$  <sup>( $0.8 \cdot 10^{-3} \text{ bar}$ )</sup> and sputtering for the  
surfaces of articles to be treated was carried out by the  
discharge in an atmosphere of the introduced gas at  $500^{\circ}\text{C}$  for  
10 0.5 hour for Test No. 16 and for 1 hour for Test No. 17.

Nitrogen( $\text{N}_2$ ) gas was used as the nitriding gas in the  
ion nitriding step and the nitriding was carried out under  
treating conditions as shown in Table 4.

Thus, a black aluminum nitride layer was formed on the  
15 surface of each article. The thickness of aluminum nitride  
layers thus obtained was measured. The results are shown in  
Table 4.

Table 4

20

Test No.	Ion nitriding treatment condition			Layer thickness ( $\mu\text{m}$ )
	Gas pressure (bar) Torr	Nitriding temp. ( $^{\circ}\text{C}$ )	Treating time(hr)	
16	( $4.67 \cdot 10^{-3}$ ) 3.5	500	5.0	3.0
17	( $2.67 \cdot 10^{-3}$ ) 2.0	450	5.0	2.0

25

Further, the articles subjected to ion nitriding treatment  
were tested for wear resistance. For comparison, non-treated

1 specimens having the same quality and dimensions as those of  
the treated articles were similarly tested for wear resistance.  
The results are shown in Fig. 4 for the specimen of Test No. 16  
and in Fig. 5 for the specimen of Test No. 17. As shown in  
5 these Figures, the both specimens of Test Nos. 16 and 17 show  
the wear amount of 1/5 or less as compared with the correspond-  
ing non-treated ones, and the aluminum nitriding proves to be  
effective to wear resistance.

Then, the article (Test No. 16) subjected to ion nitriding  
10 was tested for oxidation to examine the wear resistance property.  
The oxidation test was carried out by heating the article in an  
atmosphere at 500°C for 20 hours, and the same wear resistance  
test as in the above Example was carried out. As a result,  
the treated article subjected to the oxidation test only had  
15 the wear loss of 0.05 mm<sup>3</sup> and thus showed the similar wear  
resistance to that of the article not subjected to the oxidation  
test. Therefore, it was confirmed that the aluminum nitride  
layer was not deteriorated by oxidation.

#### 20 Example 5

Industrial pure aluminum and industrial aluminum alloys  
were used as articles to be subjected to ion nitriding, and the  
measurement of the thickness of the aluminum nitride layers  
formed and the hardness test for sections including such layers  
25 were carried out.

The ion nitriding process and apparatus used in this  
Example were similar to those in Example 1. Therefore, difference

0158271

1 between the both are described in detail.

Disk-shaped members having an outer diameter of 19 mm and a thickness of 10 mm (Test Nos. 18-22) which were made of aluminum and aluminum alloys as shown in Table 5 were used as  
5 the articles to be treated.

In the activation treatment, argon gas was introduced into the furnace, the flow of argon gas was controlled to set the argon gas pressure at  $0.6 \cdot 10^{-3}$  bar (0.8 Torr), and then sputtering was carried out by the discharge at 500°C for 1 hour.

10 In the ion nitriding treatment, nitrogen gas was introduced into the furnace, the flow of nitrogen gas was controlled to set the nitrogen gas pressure at  $6.67 \cdot 10^{-3}$  bar (5 Torr), and then the ion nitriding was carried at 475°C for 10 hours.

Thus, a black aluminum nitride (AlN) layer was formed on  
15 the surface of each article. The thickness of aluminum nitride layers thus obtained was measured. The results are shown in Table 5. The section of each treated article was polished obliquely to measure the sectional hardness. The results are also shown in Table 5. As a result of the sectional hardness  
20 test, all treated articles showed a hardness of above Hv 2000.

Table 5

Test No.	Material to be treated(JIS)	Layer thickness( $\mu$ m)	Surface hardness(Hv)
18	1050	4.0	2150
19	2017	5.0	2050
20	5052	6.0	2300
21	6061	3.2	2100
22	7072	3.5	2050

1 WHAT IS CLAIMED IS:

1. A process for ion nitriding aluminum or aluminum alloy as an article to be treated, comprising the steps of  
5 disposing said article to be treated in a sealed vessel;  
removing the residual oxygen gas in said vessel;  
heating the surface of said article to a prescribed nitriding temperature by introducing a heating gas into said vessel and causing discharge therein;  
10 activating the surface of said article by introducing an activating gas into said vessel and causing discharge therein;  
and  
ion nitriding the surface of said article by introducing a nitriding gas into said vessel and causing discharge therein,  
15 thereby forming an aluminum nitride layer having high hardness and wear resistance.

2. A process according to Claim 1, wherein  
said activating gas is at least one rare gas selected  
20 from the group consisting of helium, neon, argon, krypton, xenon and radon.

3. A process according to Claim 2, wherein  
said discharge in the activating step is one of direct  
25 current glow discharge, alternating current glow discharge and ion beam sputtering.

4. A process according to Claim 3, wherein  
the pressure in said vessel in the activating step is

1 in the range of from  $10^{-3}$  to 5 Torr ( $1.33 \cdot 10^{-6}$  to  $6.67 \cdot 10^{-3}$  bar).

5. A process according to Claim 2, wherein  
said nitriding gas is selected from nitrogen gas, ammonia  
5 gas and a mixed gas of nitrogen and hydrogen.

6. A process according to Claim 5, wherein  
said discharge in the ion nitriding step is one of direct  
current glow discharge and alternating current glow discharge.  
10

7. A process according to Claim 6, wherein  
the pressure in said vessel in the ion nitriding step  
is in the range of from  $10^{-1}$  to 20 Torr ( $1.33 \cdot 10^{-4}$  to  $2.67 \cdot 10^{-2}$  bar).

15 8. A process according to Claim 1, wherein  
the ion nitriding step is carried out at a temperature  
ranging from 300 to 550°C.

20 9. A process according to Claim 1, wherein  
said residual oxygen gas is removed by repeating a  
series of the reduction of pressure in said vessel and the  
subsequent replacement of the residual oxygen gas by a gas  
introduced therein, and  
said ion nitriding step is carried out at a temperature  
25 ranging from 300 to 550°C.

10. A process according to Claim 9, wherein  
said reduction of pressure is carried out by a vacuum pump

0158271

1 selected from a rotary pump and a combination of a rotary pump  
and a diffusion pump.

11. A process according to Claim 10, wherein  
5 said introduced gas in the removing step is one of hydrogen  
gas and a rare gas, and

said ion nitriding step is carried out at a temperature  
ranging from 300 to 550°C.

10 12. A process according to Claim 2, wherein  
said heating gas in the heating step is selected from  
hydrogen gas, nitrogen gas and a rare gas, and  
said ion nitriding step is carried out at a temperature  
ranging from 300 to 550°C.

15 13. A process according to Claim 13, wherein  
said discharge in the heating step is one of direct current  
glow discharge and alternating current glow discharge.

20

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4/3

1/3

0158271

Fig. 1

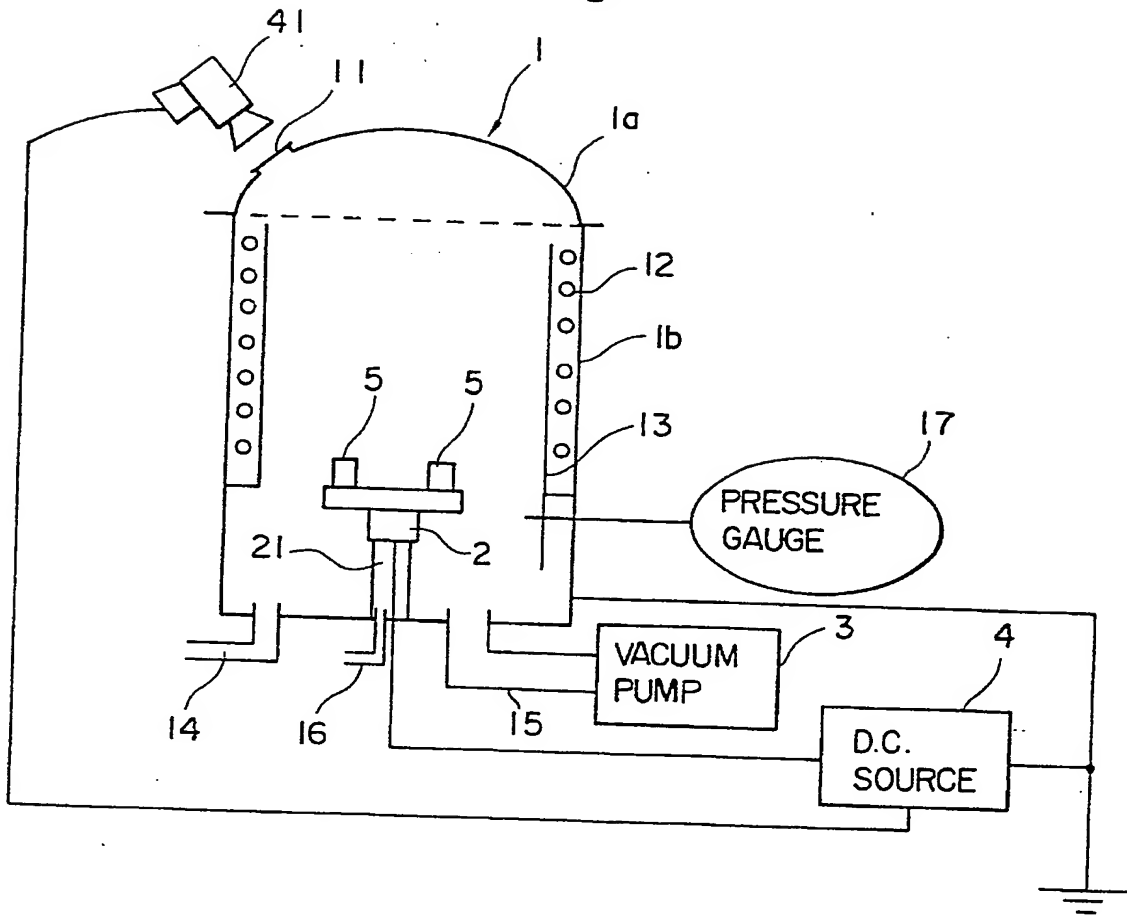
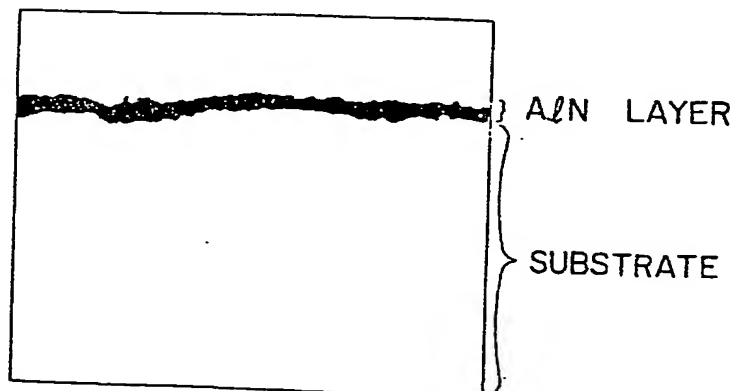


Fig. 2





7/5

0158271

Fig. 3

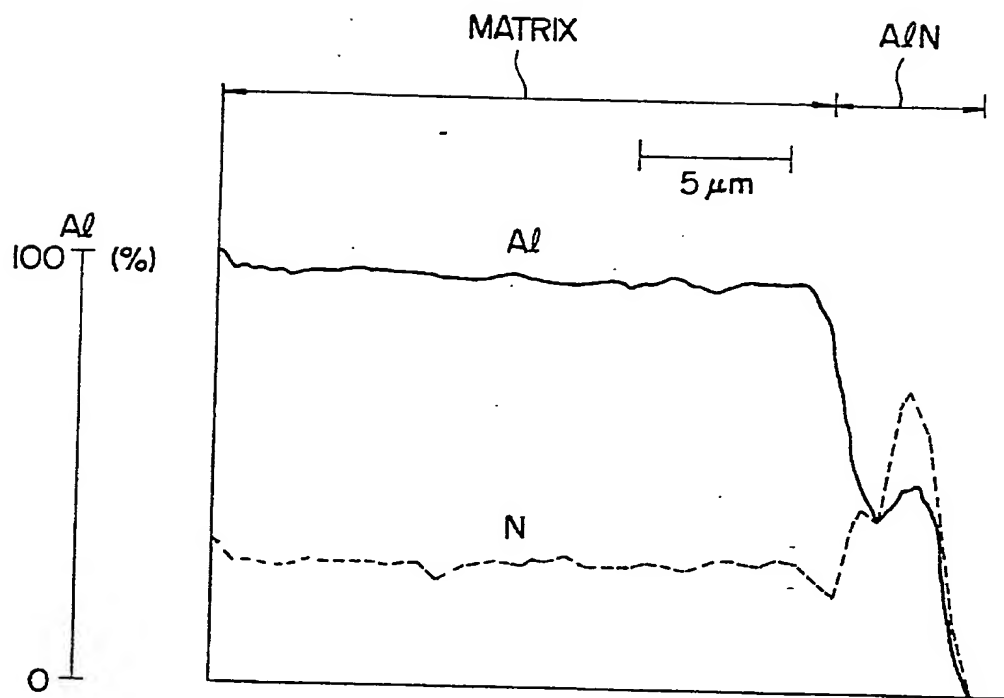
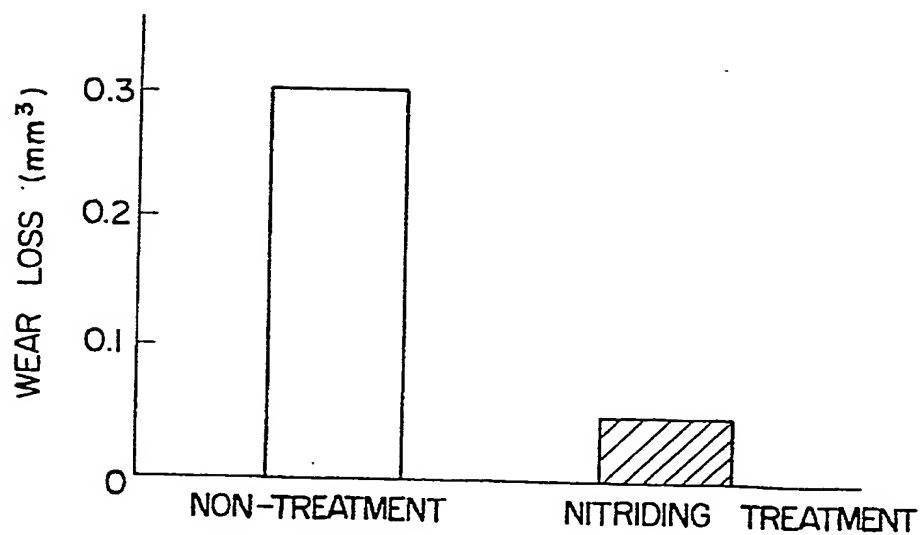


Fig. 4



3/3

0158271

3/3

0158271

Fig. 5

